

Structure of $V_2O_5 \cdot nH_2O$ Xerogel Solved by the Atomic Pair Distribution Function Technique

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The structure of most materials can be determined because they can be crystallized and thus studied by a technique called crystallography. But disordered materials lack the periodicity of crystals and show diffraction patterns that are much more diffuse. Scientists from BNL and Michigan State University have successfully applied a technique called atomic pair distribution function at NSLS beamline X7A to determine the structure of the $V_2O_5 \cdot nH_2O$ xerogel, a disordered material that could be used in chemical sensors, fast switching devices, and reversible lithium ion batteries.

The $V_2O_5 \cdot nH_2O$ xerogel, an organic polymer that can swell in suitable solvents to yield particles possessing a network of polymer chains, has fascinated researchers for many decades and inspired an intensive search for potential applications, such as chemical sensors, fast switching devices, and reversible lithium ion batteries. Despite decades of experimentation with this xerogel, its atomic structure has remained somewhat of a mystery because it does not form crystals but exists only as ribbon-like particles about 10 nanometers wide and one micrometer long, as shown in **Figure 1**.



Authors (from left): Valeri Petkov, Pantelis Trikalitis, and Mercouri Kanatzidis

The limited diffraction pattern of $V_2O_5 \cdot nH_2O$ makes it impossible to determine its three-dimensional structure using traditional crystallographic techniques. But the pattern contains a small number of features that indicate the presence of intermediate-range order and a pronounced diffused component. These are characteristics of “nanocrystalline” materials that have well-ordered local structures limited to the nanometer-length scale.

Scientists have put forward two competing structural models for $V_2O_5 \cdot nH_2O$. Jacques Livage of the University of Paris VI proposed that the xerogel, on the atomic scale, is a stack of corrugated single layers of VO_5 units, with the layers closely related to those occurring in crystalline V_2O_5 . On the other hand, Y. Oka of Kyoto University proposed that the xerogel is made of V_2O_5 bilayers according to the crystalline structure of either $Na_x V_2O_5$ or $K_x V_2O_5$ (where x is an integer). But neither model can fully explain experimental observations made using the x-ray diffraction technique nor describe the atomic structure in terms of a unit cell and atomic coordinates.

We have determined the three-dimensional structure of $V_2O_5 \cdot nH_2O$ using the atomic pair distribution function (PDF) technique, which has emerged recently as a powerful and unique tool for the structural characterization of crystalline materials with significant disorder. The strength of the technique is that it takes into account all components of the diffraction pattern and thus reflects the longer-range structural order and the local deviations from it. The technique is gaining importance because of the availability of high energy, high flux synchrotron sources, such as the NSLS, that make accurate and fast data collection possible.

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We have shown that the structure of $V_2O_5 \cdot nH_2O$ can be well described as an assembly of almost perfect bilayers of single V_2O_5 layers made of square pyramidal VO_5 units with water molecules residing between them, as shown in **Figure 2**. The stacking sequence is imperfect because of the extensive turbostratic disorder in this material, meaning that the layers are stacked in one direction, but rotated every one way in the other two, similar to a deck of cards that has not been straightened after a game.

This structure explains almost all known spectroscopic, physical, and chemical properties of the material, and reveals the atomic ordering in the individual ribbon-like particles, as shown in **Figure 3**.

The most important outcome of the study is that it yields the three-dimensional structure of nanocrystalline $V_2O_5 \cdot nH_2O$ in terms of a relatively simple model with only few meaningful parameters, such as its unit cell and symmetry. This work also shows that, even with a very low degree of structural coherence, at synchrotrons such as NSLS, using the right techniques, it is possible to determine nanoscale structures at the atomic level.

Although the PDF technique is not an *ab initio* structure determination technique, it can successfully distinguish between different structural possibilities, giving both local and long-range structural information.

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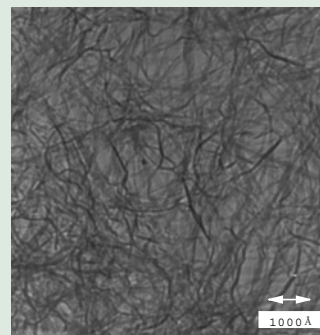


Figure 1. Transmission electron microscopy image of the $V_2O_5 \cdot nH_2O$ xerogel.

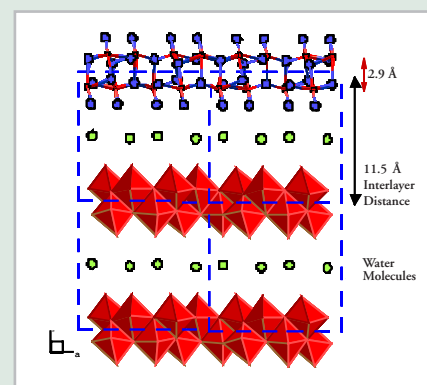


Figure 2. Structure of $V_2O_5 \cdot nH_2O$ xerogel (polyhedra and ball-stick model), as revealed by using the atomic pair distribution function technique. Characteristic distances are shown. Water molecules are shown in green.

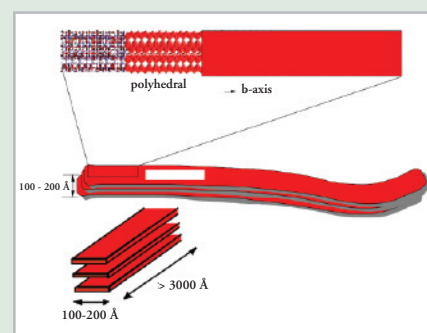


Figure 3. Ribbon-like representation of $V_2O_5 \cdot nH_2O$ xerogel showing intermediate structural makeup and overall V_2O_5 slab organization.